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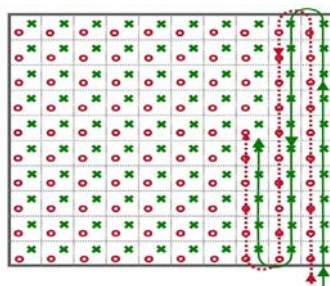
Environmental Science and Technology Certification Program

Incremental Sampling Methodology (ISM) for Metallic Residues

Project ER-0918

Jay L. Clausen, Thomas Georgian, and Anthony Bednar

August 2013



ISM sampling design, increment collection, milling, digestion, and analysis.

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Incremental Sampling Methodology (ISM) for Metallic Residues

Project ER-0918

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Abstract

Heterogeneous distribution of metallic residues in surface soils creates unique challenges for collecting soil samples that provide representative and reproducible results. In particular, soils containing metal fragments at military training ranges, such as small-arms ranges, are especially problematic to analyze owing to their large compositional and distributional (i.e., spatial) heterogeneities. The recognition of the heterogeneous nature of energetic residues in surface soils at military training ranges resulted in significant changes to the field sampling and sample processing procedures for energetics as described in United States Environmental Protection Agency (USPEA) SW-846 Method 8330B. The incremental sampling methodology (ISM) of Method 8330B for energetics was modified to develop a similar approach for metals. The approach has been successfully implemented to analyze surface soils with metallic residues at several active and inactive military training ranges. In most cases, ISM produced results more representative and reproducible than results from conventional grab (i.e., discrete) sampling and analysis procedures for surface soils collected from small-arms ranges containing metallic residues.

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Preface

This study was conducted for the Environmental Science and Technology Certification Program (ESTCP) under Project ER-0918, *Demonstration of the Attributes of Multi-Increment Sampling and Proper Sample Processing Protocols for the Characterization of Metals on DoD Facilities*. The technical monitor was A. Leeson, Program Manager for the Environmental Security and Technology Certification Program.

This report was prepared by Jay Clausen (Biogeochemical Sciences Branch, Dr. Terry Sobecki, Chief) at the US Army Corps of Engineers (USACE) Engineer Research and Development Center (ERDC), Cold Regions Research and Engineering Laboratory (CRREL) in Hanover, New Hampshire (ERDC-CRREL); Anthony Bednar at the ERDC Environmental Laboratory (EL); and Thomas Georgian USACE, Environmental and Munitions Center of Expertise (EM CX). At the time of publication, Dr. Justin Berman was Chief of the Research and Engineering Division. The Deputy Director of ERDC-CRREL was Dr. Lance Hansen, and the Director was Dr. Robert Davis.

Special thanks go to Dr. Andrea Leeson, Dr. Jeffrey Marquess, and all the ESTCP panel members and technical advisors for the advice and technical review that they have provided.

This report is dedicated to Alan Hewitt our colleague who conceived of this project. He is admired for his enthusiasm and energy for scientific research and whose contributions will endure.

COL Jeffrey R. Eckstein was the Commander of ERDC, and Dr. Jeffery P. Holland was the Director.

Nomenclature

Al	Aluminum
B	Boron
Ba	Barium
Cd	Cadmium
Ce	Cerium
CMIST	CRREL Multi-Increment Sampling Tool
Co	Cobalt
Cr	Chromium
CRREL	Cold Regions Research and Engineering Laboratory
Cu	Copper
DoD	United States Department of Defense
DU	Decision Unit
EDTA	Ethylenediamine Tetraacetic Acid
EL	Environmental Laboratory
EM	Engineer Manual
ERA	Environmental Research Associates
ERDC	Engineer Research Development Center
ESTCP	Environmental Science Technology Certification Program
Fe	Iron
H ₂ O ₂	Hydrogen Peroxide
H ₃ PO ₄	Phosphoric Acid

HCl	Hydrochloric Acid
Hg	Mercury
HNO ₃	Nitric Acid
HPLC	High Performance Liquid Chromatography
ICP-AES	Inductively coupled plasma–atomic emission spectrometry
ICP-MS	Inductively Coupled Plasma–Mass Spectrometry
ISM	Incremental Sample Methodology
ITRC	Interstate Technology Regulatory Council
K	Potassium
LCS	Laboratory Control Sample
LOD	Limit of Detection
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
MSD	Matrix Spike Duplicate
Na	Sodium
NH ₄ OH	Ammonium Hydroxide
Ni	Nickel
Pb	Lead
RSD	[Percent] Relative Standard Deviation (also %RSD)
Sb	Antimony
Sn	Tin
Sr	Strontium
STD	Standard Deviation

SU	Sampling Unit
Ti	Titanium
UCL	Upper Confidence Limit
USACE	United States Army Corps of Engineers
USEPA	United States Environmental Protection Agency
USS	US Standard
UTL	Upper Tolerance Limit
V	Vanadium
W	Tungsten
Zn	Zinc
Zr	Zirconium

Unit Conversion Factors

Multiply	By	To Obtain
acres	4,046.873	square meters
cubic feet	0.02831685	cubic meters
cubic inches	1.6387064 E-05	cubic meters
cubic yards	0.7645549	cubic meters
degrees Fahrenheit	(F-32)/1.8	degrees Celsius
feet	0.3048	meters
gallons (US liquid)	3.785412 E-03	cubic meters
hectares	1.0 E+04	square meters
inches	0.0254	meters
microns	1.0 E-06	meters
miles (US statute)	1,609.347	meters
ounces (US fluid)	2.957353 E-05	cubic meters
pounds (mass)	0.45359237	kilograms
square feet	0.09290304	square meters

1 Introduction

Since the publication of United States Environmental Protection Agency (USEPA) SW-846 Method 8330B (USEPA 2006a) for explosives, there have been efforts (e.g., states of Alaska and Hawaii) to develop incremental sampling methodologies (ISMs) for other analytes, particularly metals (ITRC 2012). This need is a result of the recognition that conventional sampling methodologies, such as grab (discrete) sampling, often result in non-representative samples, which yield non-repeatable or reproducible data. For small sample sizes, conventional grab sampling approaches provide virtually no information on total measurement precision. However, there are no published procedures for the laboratory processing of incremental samples for analytes other than energetic compounds. Sample collection and laboratory processing procedures using ISM depend on the nature of the analytes of interest. The laboratory procedures of Method 8330B, which were developed specifically for explosives and propellants, generally need to be modified for other analytes. For example, the drying, sieving, and milling procedures for soil samples described in Method 8330B would be inappropriate for volatile organic compounds. Depending on the types of analytes of interest, milling can bias analytical results because of analyte volatilization losses or the addition of spurious contaminants. However, because milling increases precision, the larger improvements in precision may outweigh the magnitude of the biases. Prior to using ISM, during project planning, one must consider on a case-by-case basis the project's data quality objectives, the nature and concentration of the analytes, and the environmental media of interest.

There is a growing recognition within the Department of Defense (DoD) and in Federal and State agencies that protocols similar to Method 8330B are needed for the characterization of metallic residues in training ranges and in other locations. Consequently, states, such as Alaska and Hawaii, and other organizations (USEPA and the Interstate Technology Regulatory Council [ITRC]) have developed or are in the process of developing guidance for collecting ISM samples.

Military munitions use a variety of metals. For example, the casing materials for most artillery and mortar projectiles consist of iron (Fe) and manganese (Mn). The predominant metal in the anti-tank rocket is aluminum

(Al). The metals of interest at small-arms ranges are primarily antimony (Sb); copper (Cu); lead (Pb); zinc (Zn) (Clausen and Korte 2009a); and in some situations, tungsten (W) (Clausen and Korte 2009b; Clausen et al. 2010a, 2007). Pyrotechnic devices contain metal constituents, such as Al, Sb, barium (Ba), boron (B), cerium (Ce), chromium (Cr), Cu, Fe, Pb, magnesium (Mg), Mn, potassium (K), sodium (Na), strontium (Sr), titanium (Ti), W, zirconium (Zr), and Zn (Clausen et al. 2012a). As munitions containing metals are frequently used on Army training ranges, metallic residues deposited by munitions can accumulate in soils. Although the deposition of metallic residues at military ranges has only been studied on a limited basis, like explosives, metallic residue deposition is largely spatially heterogeneous (Clausen and Korte 2009a; Clausen et al. 2013, 2012a,b, 2007). Anthropogenic metallic residues are heterogeneously distributed at training ranges as particles of various sizes, shapes, and compositions (Fig. 1 and 2). To obtain representative samples (i.e., to ensure mean contaminant concentrations in the samples will be similar to the mean concentrations in the environmental population) and repeatable and reproducible estimates of the population means, the sampling design and laboratory preparation methods need to address compositional and distributional heterogeneities.

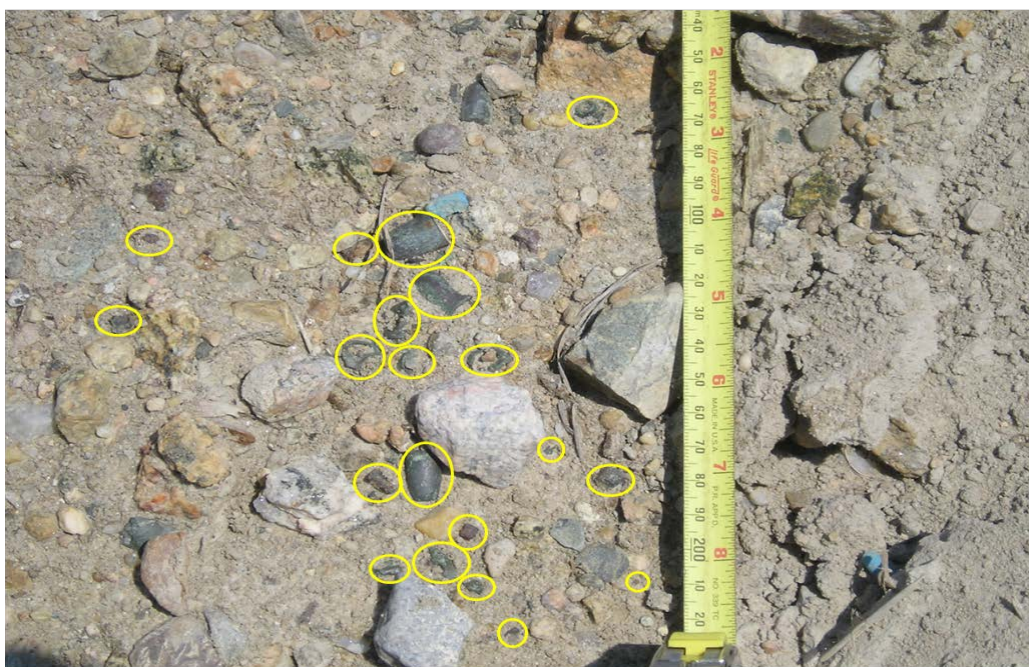


Figure 1. Metallic bullet fragments (yellow circles) and nylon cores for plastic bullets (blue material in photograph) at a small-arms range at Camp Edwards, MA.

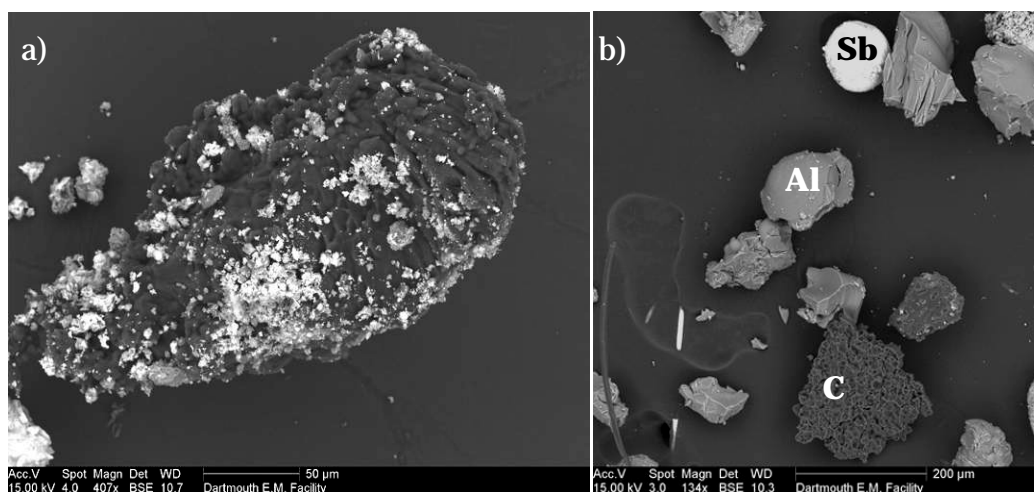


Figure 2. Residue deposited by a M117 Booby Trap Simulator: a) backscattered electron image of a carbon grain with attached metal particulates; b) image showing carbon grains, an aluminum oxide sphere, and an antimony sphere.

The current document outlines a possible protocol for ISM implementation at sites where metallic residues are present in surface soils, such as at small-arms ranges. The protocol is based on a series of studies conducted from 2009 to 2011 at small-arms ranges. These studies systematically tested and evaluated different aspects of ISM for improvements to total measurement precision and documented the findings in Clausen et al. (2012a). Following the development of an apparently acceptable ISM protocol, the studies demonstrated the process at three different military installations and compared the results to the conventional grab sampling methodology, documenting the results in Clausen et al. (2013). In general, the ISM data exhibited lower variances, biases, and outliers and improved precision and reproducibility as compared to grab samples (Clausen et al. 2013). However, there were instances where ISM did not meet the established performance criteria (e.g., for Cu). In those instances, assessment of the source of error and subsequent modifications to the ISM process would likely have resulted in meeting the performance objectives.

In addition, Clausen et al. (2012a) successfully used the methodology to assess the impact of metallic residues resulting from training with military pyrotechnics. The approach discussed may have application beyond small-arms range sites.

The objective of ISM is to obtain for analysis a single sample or replicate samples representing the mean analyte concentration representative of the Decision Unit (DU). The ISM approach reduces data variability, improves precision, and generally provides an unbiased estimate of the analyte concentration in a specified volume or mass of soil (i.e., DU) (ITRC 2012).

2 Project Planning for Implementing ISM

Very well defined Data Quality Objectives usually need to be established during project planning to successfully implement ISM. Key elements that need to be addressed during the planning phase include

1. The conceptual site model.
2. The project's objectives.
3. The tolerances for decision errors.
4. The spatial boundaries of each DU.
5. The sampling depths.
6. The number of increments per sample.
7. The number of samples per DU.

One should not physically collect soil samples from the field until the planning phase has been completed and all of the dimensions of all of the DUs have been well defined. As used in this document, the term “DU,” which is also commonly referred to as the “Sampling Unit” (SU), refers to an environmental population (e.g., some specified volume or mass of soil) that will be sampled and represented by a set of random, independent, incremental samples.

This document does not address how to establish DUs during systematic project planning (e.g., to evaluate risk from munitions constituents). However, it includes Section 3.1, *Decision unit determination*, to illustrate how historical knowledge of site activities (e.g., the expected spatial distributions of munitions constituents) can be used to stratify a site into a set of potential DUs. ITRC (2012) provides a more detailed discussion of project planning for collection of ISM samples. For general guidance on systematic planning, refer to the US Army Corps of Engineers (USACE) Engineer Manual (EM) *Technical Project Planning* (USACE 1998) and EPA QA/G-4, *Guidance on Systematic Planning Using the Data Quality Objectives Process* (USEPA 2006b). As noted in ITRC (2012), one cannot overstate the role of thorough planning for successfully implementing ISM.

Table 1 provides a brief overview of components of ISM for metals and explosives. This document primarily focuses on the field implementation and sample processing components of ISM. Environmental practitioners

should be familiar with a number of the activities summarized in Table 1 as many are done for conventional grab sampling and analyses. Some of the key differences between conventional grab sampling and ISM are the need to define the spatial boundaries (e.g., volumes) of each DU, the number of increments that will be collected for each sample, the total number of samples collected for each DU, and the more extensive laboratory sample preparation procedures. Milling performed with metallic grinding equipment warrants additional steps, such as an assessment of possible cross-contamination. At the present, it is not clear what to do with the oversize fraction, greater than 2 mm, that by USEPA definition does not constitute a soil. If desired, the metal fragments can be separated from the rock material and weighed separately. At a minimum, we recommend that material greater than 2 mm be weighed and retained for possible future additional analysis.

Table 1. Some considerations for implementing the incremental sampling methodology.

Project Stage	Specific Activity		
Project Planning	Conceptual site model		
	Determination of investigation objectives		
	Identification of the quantity and quality of data needs		
	Decision Unit identification (e.g., area and depth)		
	Number of increments per sample		
	Mass of each increment and of each sample		
Field Implementation	Selection of sampling tools		
	Collection of soil sample		
Sample Processing	Air drying		
	Sieving		
	Particle size reduction (milling)		
	Less than 2 mm (examined)		Greater than 2 mm (archived)
	Splitting (if necessary)		
	Subsampling		
	Metals digestion	Energetics extraction	
Analysis	ICP-MS or ICP-AES	HPLC	

ICP-MS—inductively coupled plasma–mass spectrometry

ICP-AES—inductively coupled plasma–atomic emission spectrometry

HPLC—high performance liquid chromatography

3 Field Implementation Using ISM

Field sampling and laboratory analytical procedures must allow for acquiring an adequate number of particles of the constituents of interest in each sample and ensure that the proportions of the various particles in the samples are similar to the proportions in the environmental populations (e.g., so the mean contaminant concentrations in the samples will be similar to the average concentrations in the population sampled). Substantively, the same field sampling strategies may be used for metallic residues as for energetics. Instead of collecting and analyzing individual grab (discrete) samples and integrating the results over an area of interest or DU or assuming that a single point represents the entire area, samples are prepared by combining a number of increments of soils from the DU to obtain an approximately 1-kg sample.

3.1 Decision Unit determination

The DU boundary is typically determined during the systematic planning stage and takes into consideration the study objectives, soil type, analyte of concern, etc. Figure 3 shows a typical configuration in the case of a small-arms range.

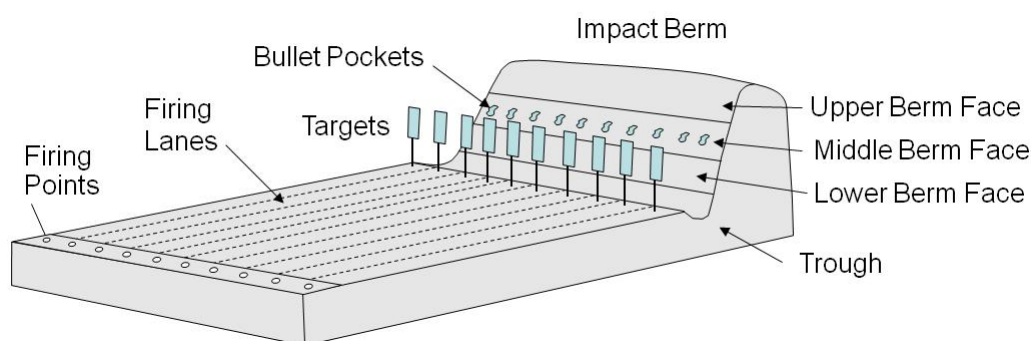


Figure 3. Configuration of a small-arms range.

In many cases, the focus of the environmental investigation is primarily on Pb and associated metals in the impact berm located behind the targets. In some instances, the metal load at the firing point and on the range floor may be of interest. As the propellant concentrations at the firing point may be of interest, sampling at firing points may also be desired. Figures 4 and 5 depict the location and configuration of three DUs for a small-arms

range with identifiable firing points, range floor, and berm face. In this example, the DU boundary extends the width of the range and encompasses all firing lanes. The Firing Point DU extends a couple meters behind the firing point and several meters down range. The Impact Berm DU encompasses the entire height of the berm. The area between the Impact Berm and the Firing Point DUs is referred to as the Range Floor DU. Based on past work of Clausen and Korte (2009a) and Clausen et al. (2012b, 2013, 2007), the only appreciable metal loading occurs at the Impact Berm.

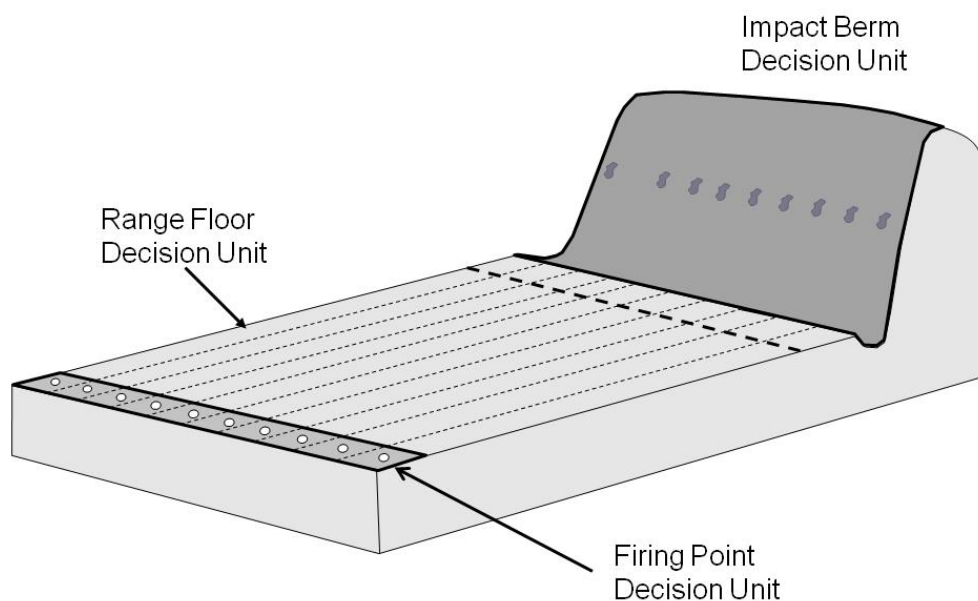


Figure 4. Possible Decision Units for small-arms ranges.

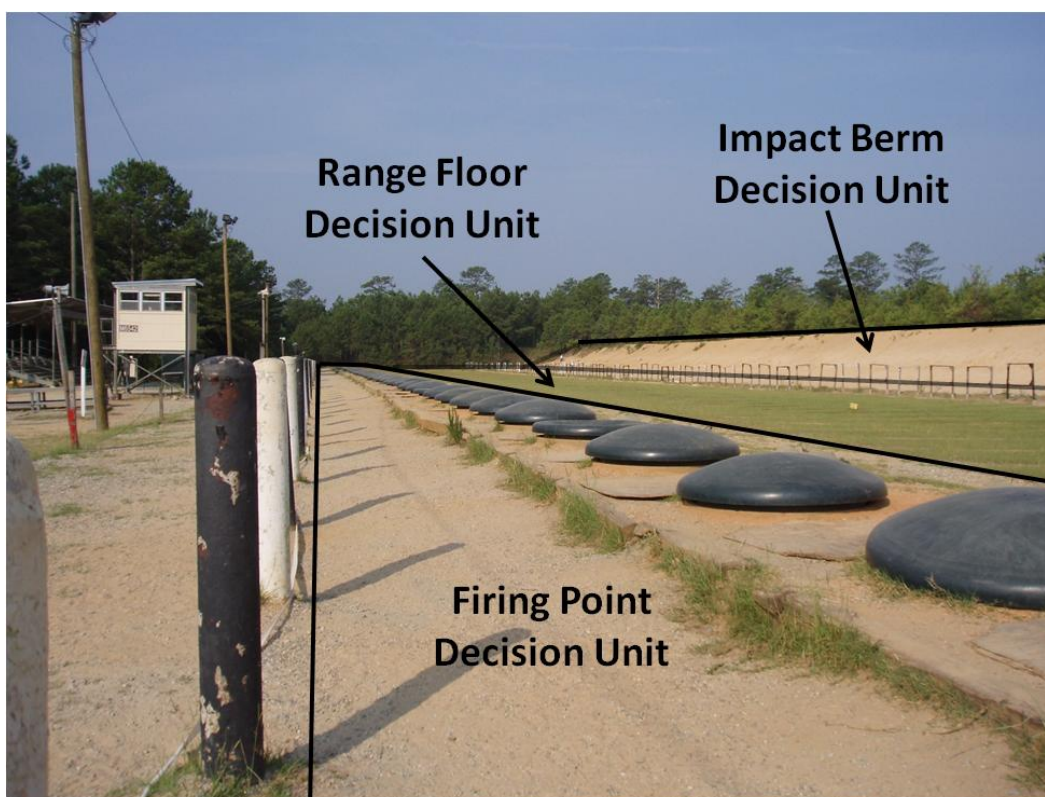


Figure 5. Example of a small-arms range with Decision Units denoted.

In some cases, it may be desired to subdivide the Impact Berm into smaller DUs. Figure 6 represents an example where greater detail was needed such that the Impact Berm DU (Fig. 5) was subdivided into ten SUs, and the Range Floor DU was subdivided into three SUs. Again, the number and size of DUs and SUs depends on a number of variables, such as the project objectives, site conditions, anticipated decisions, etc.

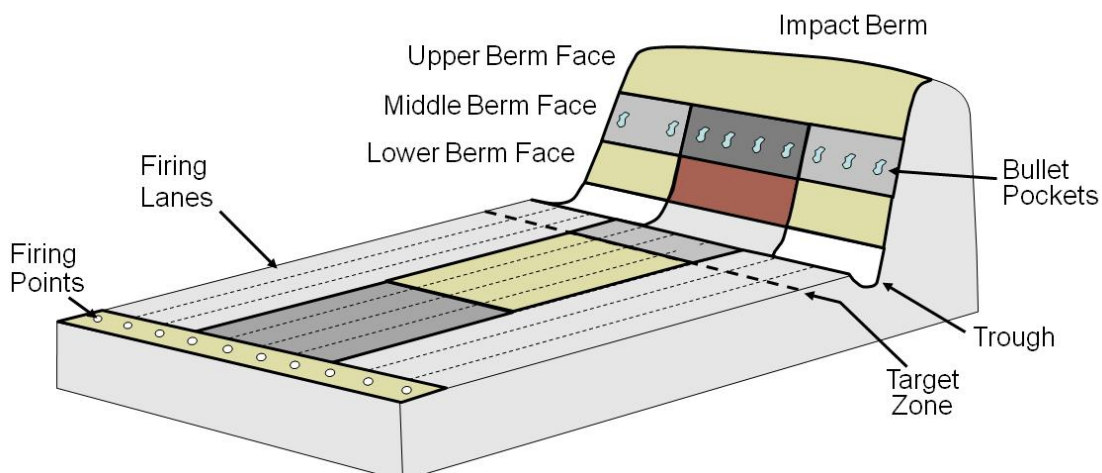


Figure 6. Subdivision of Decision Units into smaller Sampling Units for a small-arms range.

In some configurations, the small-arms range does not have contiguous berms; rather, each firing lane has its own berm (Fig. 7). In this case, it may be desirable to sample the individual berms collectively as a single DU.



Figure 7. Example of non-contiguous small-arms range impact berms.

Range boundaries may not be readily observable for older small-arms ranges. Proper project planning addressing this issue allows a sampling approach to meet the project objectives.

Besides small-arms ranges, the information in this document may also be applied to any sites where metallic residues are expected, such as grenade, anti-tank rocket, or artillery and mortar impact areas or training areas. The DU configuration will depend upon the objectives and the other information mentioned in Section 2. Figure 8 presents an example for a pyrotechnic study where the media sampled was snow and the residue was readily visible on the snow. The DU was the visible boundary between the impacted and unimpacted snow (Fig. 9). Within the DU, several smaller SU were designated to assess the concentration of metallic residues with distance from the source. There are no “wrong” DU configurations as long as the generated data meet the project needs.

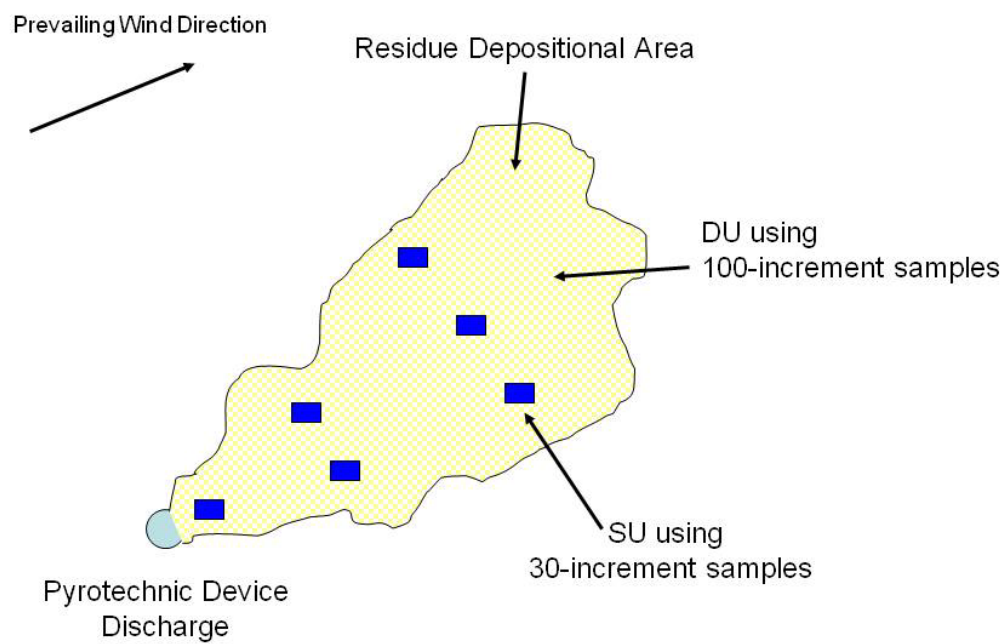


Figure 8. Example of Decision Unit (DU) and sampling unit (SU) configuration for a study of pyrotechnic metallic residue deposition on snow.

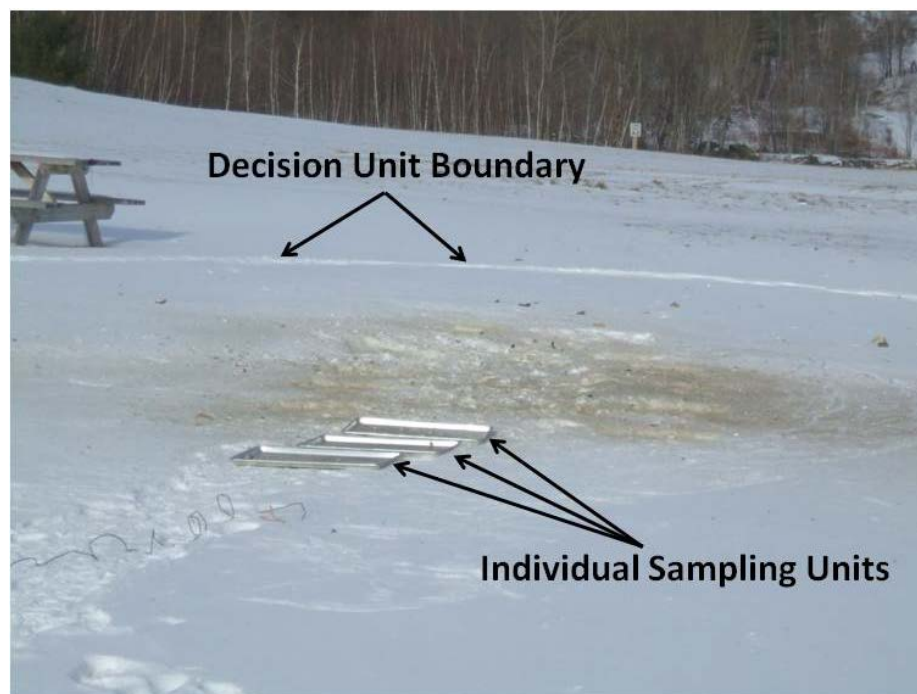


Figure 9. Example of snow impacted by pyrotechnic device detonation.

3.2 Field sampling

Once the DU is identified, distributional heterogeneity can be addressed by collecting a 1- to 2-kg incremental sample (Fig. 10) prepared from at

least 30–100 “increments” (Fig. 11) that are collected randomly over the entire DU using the systematic random approach. The objective of ISM is to obtain a proportional amount of residue particles of every composition and shape.



Figure 10. Example of an individual increment.



Figure 11. Example of a sample consisting of 100 increments.

The increments can be collected using simple random sampling, random within grids, or systematic random sampling (Fig. 12) although the preferred approach is a systematic random design (ITRC 2012). For systematic random sampling, a random starting point is selected; and the sampler

walks back and forth from corner to corner of the DU, collecting evenly spaced increments (Fig. 13). The number of increments and the sampling design is determined during project planning.

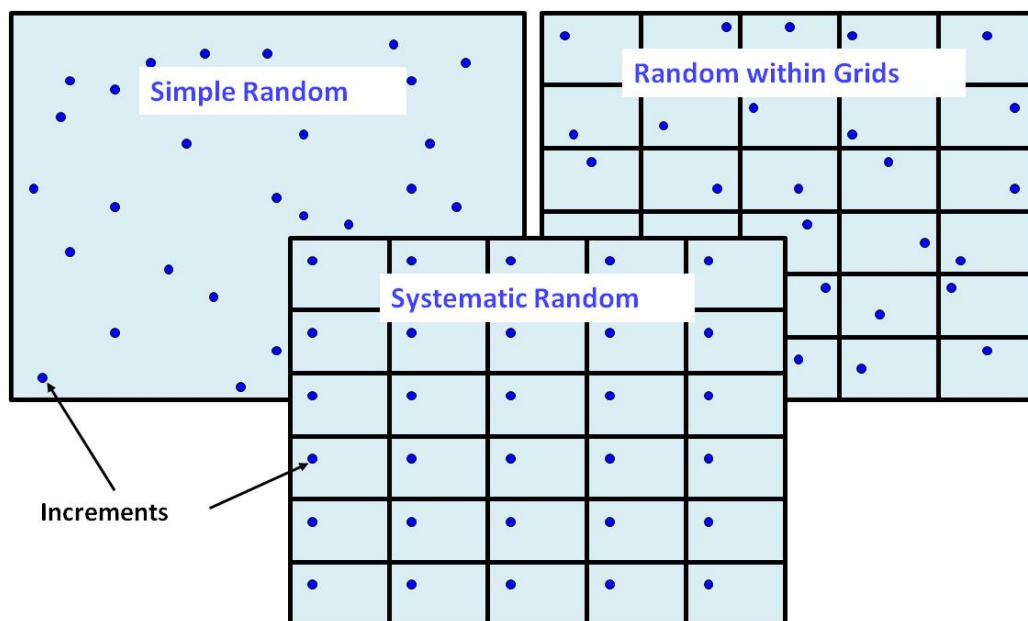


Figure 12. Comparison of simple random, random within grids, and systematic random sampling Decision Units.

The “increments” that are combined to prepare each incremental sample typically refer to cylindrical soil cores that are collected using a coring device, such as the “CRREL Multi-Increment Sampling Tool” (CMIST) shown in Figure 14 (Walsh 2009). The diameter of the sampling tool should be at least three times the diameter of the largest size fraction (Pitard 1993). Non-cylindrical devices, such as scoops, are not recommended because they have a tendency to bias the sample (e.g., more mass is removed at the surface than at depth). In addition, it is difficult to obtain a consistent volume of soil from increment to increment with scoops. ITRC (2012) presents a more in-depth discussion of sample tool selection.

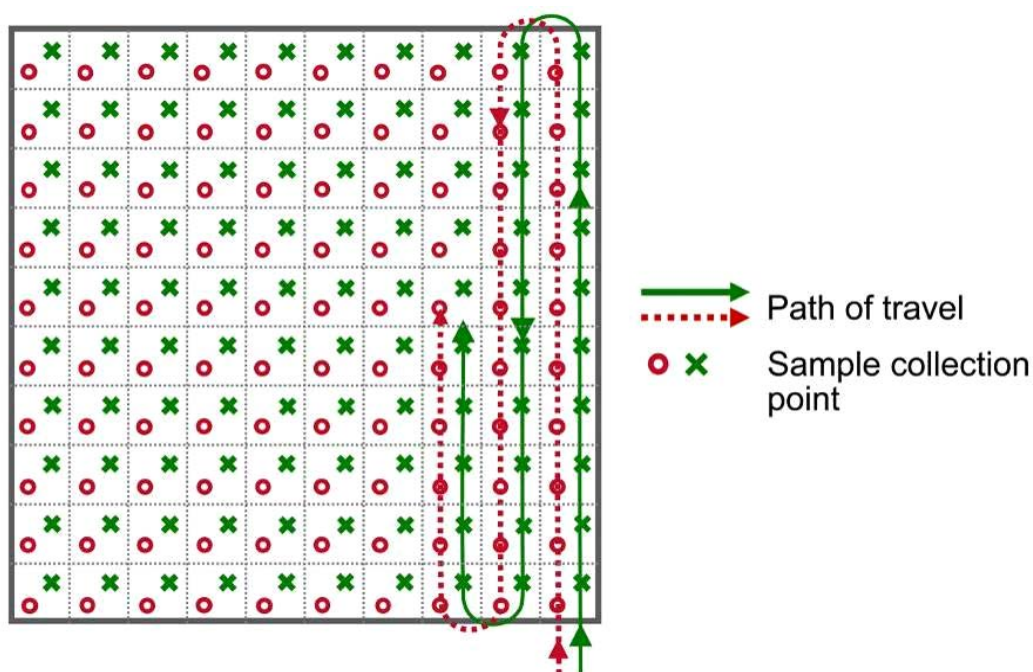


Figure 13. Example of multi-increment sampling using a systematic-random sampling design for collecting two separate 100-increment samples.

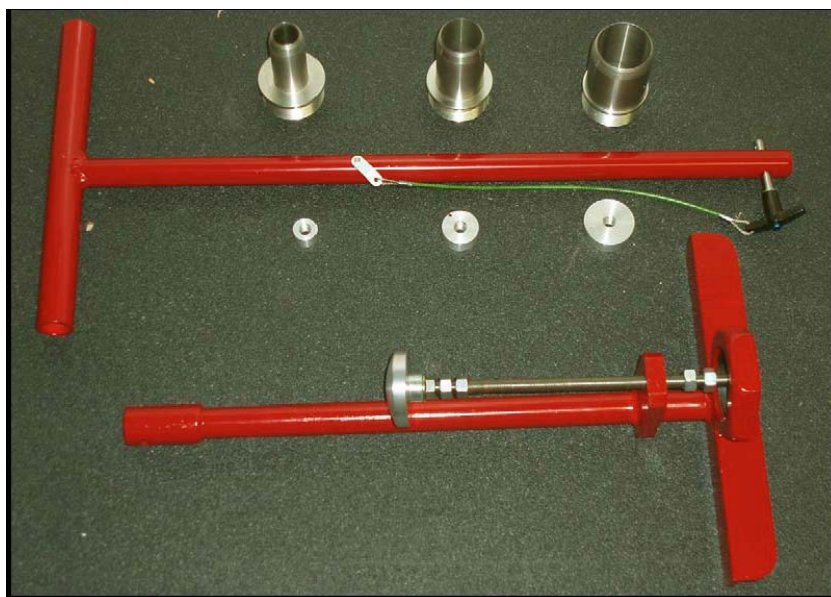


Figure 14. The CRREL Multi-Increment Sampling Tool (CMIST). Coring tips are 2-, 3-, and 4-cm diameter (left to right). Corresponding disks are shown below the handle (Walsh 2009).

For small-arms ranges, a recommended surface soil sample depth is 5 cm as the preponderance of metallic residues are found in this interval, resulting in the highest soil concentrations (Clausen et al. 2013, 2012a,b, 2010, 2007; Clausen and Korte 2009a,b). However, it is recognized that data needs established at the project planning stage will drive the sampling

depth needed to achieve project objectives. Subsurface sampling using ISM is possible but can be a time intensive process. It is critical to determine during project planning the number of replicate ISM samples required for each DU. At least three independent replicate ISM samples are typically needed to assess the total variability of the mean metal concentrations or to perform a calculation of the upper confidence of the mean (UCL). Three replicates are acceptable in situations where large deviations from normality of the sample population are not expected (ITRC 2012). At least eight replicates are recommended when the variability needs to be quantified at a higher level of confidence and non-normality (i.e., a skewed population distribution) of the sample population is expected (Matzke et al. 2007; USEPA 2009, 2007). A situation where this may occur is when upper confidence limit calculations or background studies are being conducted and compared.

The adequacy of the precision of replicate ISM results from a DU also needs to be evaluated with respect to the objectives established during project planning. In particular, the results from a set of replicate ISM samples are often used to calculate a percent relative standard deviation (RSD); and precision is often qualitatively considered acceptable when the RSD is less than 30%. However, the RSD is not a measure of usability. The RSD is a descriptive statistic that measures precision based on the variance and standard deviation. Higher RSD means poorer data quality; however, higher RSD does not always mean poorer data usability. A large RSD is indicative of large variability (relative to the mean) and a distribution that is not normal. For example, the amount of acceptable variability for replicate samples will usually depend on the magnitude of the analyte concentrations relative to the levels of interest (e.g., regulatory or risk-based thresholds or action levels). Larger variability can be tolerated when samples' concentrations are much smaller or larger than the project's levels of interest as opposed to when the concentrations are near the decision limits. However, in general, the amount of variability that is acceptable should be determined by the tolerances for decision errors and the magnitude of the analyte concentrations relative to the levels of interest (e.g., regulatory or risk-based thresholds).

Replicate results that fail to achieve objectives for precision require reevaluating the entire sample process (field sampling, sample preparation, and analysis) to assess the likely source of error and, if necessary, resampling with the appropriate modifications made to the ISM process.

The recognition of the heterogeneous nature of energetic residues in surface soils at military training ranges resulted in significant changes to the field sampling and sample processing procedures for energetics described in USPEA SW-846 Method 8330B. The ISM of Method 8330B for energetics was modified to develop a similar approach for metals. In most cases, the results from this development (Clausen et al. 2012b) and subsequent demonstration (Clausen et al. 2013) produced results more representative and reproducible than results from conventional grab (i.e., discrete) sampling and analysis procedures for surface soils collected from small-arms ranges.

If metals and explosives are both contaminants of interest and separate incremental samples are not collected in the field for metals and explosives, to control distributional and compositional heterogeneities, each sample must be split in the laboratory in a manner that is consistent with Gy's sampling theory and practice (Pitard 1993). In general, if the incremental sample contains metallic residues, it is preferable to air-dry, sieve, weigh the size fractions, and mill the sieved portion of the sample prior to splitting it for digestion and instrumental analysis. If the sample is not milled, the sample will typically need to be split in the laboratory after it is air dried and sieved. Standard operating procedures to split, mill, and subsample should be developed on a project-specific basis and should be consistent with the guidance in ASTM 2003 and USEPA 2003. In general, samples should not be split in the field using a method such as cone and quartering because of its inferior performance compared with other laboratory procedures, such as using a rotary splitter (USEPA 2003).

4 Laboratory Sample Preparatory Procedures for Metals

In general, when soils contain metal particulates (e.g., bullet fragments), the entire sample should be air dried, sieved, and mechanically pulverized to reduce particle sizes. Table 2 summarizes the proposed changes to the sampling processing procedures from USEPA Method 3050B, which are referred to as proposed Method 3050C.

4.1 Drying and sieving

Incremental samples are first air-dried at room temperature (e.g., for several days) by spreading each sample evenly onto a large tray (Fig. 11). After drying, the soil sample is passed through a 2-mm (US Standard [USS] Sieve #10 mesh) sieve; and the two fractions are weighed. A 10-mesh sieve is used to separate the less-than-2-mm size fraction for extraction and instrumental analysis. At present, there is inadequate data to determine whether this is the most appropriate particle size threshold for processing soils for metal analyses; but it serves as a “default” criterion for the exclusion of pebbles, twigs, and other larger material that would typically not be categorized as “soil.” However, as has been documented, an appreciable mass of metal can be present in the less-than-2-mm fraction (Clausen et al. 2007).

If the material consists of particles of the same size and density, then once air dried, the less-than-2-mm soil fraction can be mixed and subsequently subsampled (ITRC 2012). However, in the case of metallic and energetic residue deposition, additional processing is usually necessary because of large compositional and distribution heterogeneity. As large variability arises from compositional heterogeneity (e.g., as measured by the fundamental error), subsampling procedures to minimize distributional heterogeneity, such as the use of a rotary splitter and other techniques described in ASTM 2003 and USEPA 2003), prior to milling will likely result in only marginal improvements in precision. Previous studies by Clausen and Korte (2009a) and Clausen et al. (2013, 2012b, and 2007) have demonstrated that surface soil samples at small-arms ranges exhibit a high degree of heterogeneity; and splitting these samples prior to milling yields non-reproducible results even when using a robust device, such as rotary

splitter. RSDs of over 100% are commonly observed for unmilled replicate samples.

Table 2. Salient differences between Method 3050B and Proposed Method 3050C.

Sampling Steps	Method 3050B/3051A Conventional Sampling	Proposed Method 3050C Incremental Sampling Method
Field Sampling	Not explicitly addressed in method. Typically, grab (discrete) samples are collected.	An incremental sample consists of 30–100 “increments” collected randomly over the entire DU (e.g., using systematic sampling). For cohesive surface soils, an “increment” typically consists of a small cylindrical soil core (e.g., 2–5 cm in length) collected with a 2- to 4-cm diameter coring device (e.g., as shown in Fig. 11).
Sample Mass and Containers	Approximately 200 g of soil in 4-oz, wide-mouth, amber-glass jars with screw-top lids.	Typically, 1–2 kg of soil in clean, large (e.g., 15 × 15 in., 6 mm thick) polyethylene plastic bags sealed with Ty-wraps.
Sample Drying	Sample drying is optional and is not typically done.	Sample is air-dried at room temperature by spreading onto a tray to form a thin, uniform slab.
Sieving	“...sieve, if appropriate and necessary, using a USS #10 sieve...” Soil samples are typically not sieved.	Samples are passed through a USS #10 (2 mm) sieve. Both size fractions are weighed and the less-than-2-mm fraction is additionally processed.
Milling	“Wet samples may be dried, crushed, and ground to reduce sample variability...” Milling is typically not performed.	Samples are milled using appropriate mechanical grinders, such as puck mill or roller (ball) mills. Milling must result in finely ground material of uniform appearance and texture. Recommend 5 × 60 s with 60 sec cooling period for the puck mill when metals and energetics are desired. For metals only, a cooling period is not needed. Recommend 8 hr for ball mill for metals only.
Laboratory Subsampling	“Mix the sample thoroughly to achieve homogeneity...” Soil is often stirred with a spatula or similar device (often in the original container) and a single aliquot (e.g., scooped from the top of the container) is collected and then subsampled for digestion and analyses.	After milling, the soil is spread onto a large tray to form a thin slab of material of uniform thickness. At least 20 small aliquots are randomly collected over the entire slab with a flat-bottom spatula with sides or similar device and combined to prepare a subsample for digestion and analysis.
Subsample Mass	3050B: 1–2-g wet weight or 1-g dry weight 3051A: 0.500 g	2–10-g dry weight

In addition, the compositional heterogeneity cannot be overcome by simply collecting a larger mass of material to digest (i.e., 10 g versus 1 to 2 g as called for in the present Method 3050B or 3051A) (USEPA 1996a, 2007). For example, results of small-arms range soils show that increasing the

mass of material digested prior to milling still results in large variability of the Pb concentrations (Table 3). In fact, Table 3 shows that the RSDs of the replicate subsample analyses are larger for the larger subsample masses. In addition, Table 3 also shows that the mean of the set of 2-g replicates for sample CEA37 is significantly different from the means of the 5- and 10-g replicates whereas the MI4 5-g mean is significantly different from the means of the 2- and 10-g samples. This suggests that compositing (i.e., physically combining) a large number of increments in the field alone will not necessarily provide reproducible results; additional sample processing procedures in the laboratory, such as milling, are also needed.

Table 3. Comparison of two different small-arms range soils for lead with differing mass of material digested.

Sample ID	CEA37	CEA37	CEA37	MI4	MI4	MI4
Mass Digested	2g	5g	10g	2g	5g	10g
Concentration	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Rep 1	1490	3330	2040	632	271	598
Rep 2	1380	3440	2480	602	259	566
Rep 3	1060	1680	5750	683	266	576
Rep 4	1110	2700	1340	645	278	561
Rep 5	2080	1120	2980	605	292	573
Rep 6	1130	1110	2970	679	266	592
Rep 7	1030	1220	1450	627	260	641
Rep 8	1170	1830	2850	595	263	1120
Rep 9	1210	1190	1510	657	255	613
Rep 10	1290	1570	1850	613	250	691
Rep 11	1650	5890	1780	658	257	581
Rep 12	1500	1170	3710	633	272	1160
Rep 13	1360	2320	1400	685	255	584
Rep 14	1190	3190	2110	625	258	578
Rep 15	1510	3160	1700	734	258	598
n	15	15	15	15	15	15
Mean (mg/kg)	1344	2328	2395	645	264	669
Median (mg/kg)	1290	1830	2040	633	260	592
Minimum (mg/kg)	1030	1110	1340	595	250	561
Maximum (mg/kg)	2080	5890	5750	734	292	1160
Standard Deviation (mg/kg)	276	1324	1165	38	11	194
%RSD	21	57	49	6	4	29

These data also illustrate why the failure to control heterogeneity for laboratory analyses may give misleading results when only a small number of laboratory replicate subsamples are analyzed. For example, if only replicates 9–11 of the CEA37 10-g sample had been analyzed, one would infer that the measurement uncertainty is quite low (i.e., RSD of 11%). On the other hand, if replicates 2–4 of the CEA37 10-g sample had been analyzed, the RSD is 72%. In addition, the calculated means of 1713 mg/kg for replicates 9–10 and 3190 mg/kg for replicates 2–4 are quite different.

If the end use of the data is to assess the risk of incidental ingestion of, for example, lead, the concentration of metals in larger particles may be of less interest than the metal concentrations in the finer (less than or equal to 0.25 mm) fraction. Preliminary data indicate that reasonable precision may be obtained without milling if the incremental samples are processed using smaller diameter sieves. In particular, a finer mesh sieve, such as 0.25 mm (USS Sieve #60), may be used to process incremental soils samples prior to subsampling for lead (USEPA 2000a, 2003; ITRC 2003). A finer mesh sieve will significantly improve precision as the sieved material will contain a larger number of smaller particles relative to the number of soil particles. However, it is important to note that sieving an unground sample through sieves finer than 2 mm is generally not appropriate for high explosives and propellants. Much of the mass of the energetic analytes is in particles greater than 0.59 mm (USS Sieve #30) (Walsh et al. 2007). So, this approach would likely not be appropriate for a sample collected at a firing point and to be analyzed for both energetics and metals.

4.2 Milling

Particle size reduction using milling is typically needed to obtain reproducible results for soils containing metal particles, even within the less-than-2-mm soil size fraction. Metallic particles from munitions possess a variety of sizes, densities, shapes, and compositions. Therefore, if samples are not milled, compositional heterogeneity will likely result in a large variability among the subsamples typically digested (e.g., 2–10 g) and analyzed (Table 3). Usually, sample disaggregation using a mortar and pestle will not reduce particle sizes adequately.

The milling equipment needs to be selected on the basis of the metals that are of primary interest for each project. Most commercial crushing or grinding equipment possess working surfaces composed of metal alloys containing Fe, Cr, W (carbide), etc. For example, metal contamination

from the puck mill in Method 8330B has been observed to increase sample Cr and Fe levels by multiplicative factors (Clausen et al. 2013, 2012b). This spurious contamination may be significant when the milling equipment is constructed from the same metals as the contaminants of interest in the environmental samples. This issue can be overcome by using non-metallic equipment if deemed necessary. Again, this issue should be addressed during the project planning stage, prior to collecting samples. A study by Felt et al. (2008) also found slight bias increases with non-metallic milling equipment. As non-metallic grinders were used, the positive biases seemed to be the result of surface area increases that improved metal solubilization during acid digestion (i.e., improved sample recovery). Therefore, given the small effect, separation of the cause of an increase of metal content either from increased particle surface area or cross-contamination is not easily discernible. However, milling seemed to reduce total measurement variability such that the small positive biases tended to be “off-set” by the improved precision (e.g., milling resulted in small upper 95% confidence limits of the mean owing to improved precision).

Milling equipment with non-metallic grinding surfaces is also available. The roller mill is available with Teflon lined cans and ceramic chips or agate balls. If a puck mill is desired but metal cross-contamination is a concern, non-metallic puck mills constructed of agate are also available. Presently, though, the agate bowls are a third of the size of the metal bowls, thus requiring multiple milling events to process the same volume of material. However, metal contamination from the puck mill is not typically an issue of concern for the metals of high interest at small-arms ranges (Cu, Pb, Sb, and Zn).

Acceptable results using a ring and puck mill or ball (roller) mill have been obtained from these studies of small-arms ranges (Clausen and Korte 2009a,b; Clausen et al. 2013, 2012b, 2007; Felt et al. 2008). However, as previously noted, when samples will be collected from a firing point for analysis of energetics and metals, the puck mill (USEPA 2006a) is the only suitable milling equipment that is known to date. When both propellant and metallic residues measurements are planned, a 300 s milling interval with a 60 s cooling interval between milling is needed (Clausen et al. 2012a,b). If only metal measurements are planned, a cooling step between milling intervals is generally not necessary. Satisfactory results with the ball mill were achieved using a milling interval of at least 8 hr (Clausen et

al. 2012b). In some situations, longer or shorter milling intervals may be acceptable.

There are also circumstances in which incremental samples may not be amenable to milling as some metals in elemental form (e.g., Cu and tin [Sn]) are malleable (Clausen et al. 2012b) or volatile (e.g., mercury [Hg]). As reported in Clausen et al. (2012b), although Pb is malleable, no issues were noted as a result of milling with a puck mill or roller mill. Depending on the nature of the milling equipment selected, malleable particles can smear on milling surfaces. This has been observed in some soil samples containing Cu residues (Clausen et al. 2012b). Although Pb is a soft metal, smearing and associated losses have not been an issue (Clausen et al. 2013, 2012b). Clausen et al. (2012b) tested a laboratory control sample (LCS) from Environmental Resource Associates of Golden, CO, that contained known concentrations of small-arms range metal particles of Pb, Cu, Sb, and Zn; and recoveries for Pb, Sb, and Zn were very good. However, studies by Clausen et al (2012a,b) resulted in poor precision for Cu. It is not clear if a longer milling interval would result in improved precision for Cu or if other changes, such as increasing the digestion aliquot mass or digestion interval or increasing the number of subsamples, would have improved sample precision. Also, losses of analytes to milling equipment surfaces can result in significant negative bias, such as the case for Cu. Decontamination of malleable metals from milling equipment can also be problematic, resulting in positive biases from sample-to-sample “carry over” (i.e., cross-contamination). Unfortunately, performance data for various milling equipment for incremental soil samples containing malleable metal particles other than Cu (e.g., projectile fragments in a firing range berm) are currently extremely limited for reliable conclusions. However, if soil samples containing metal particles are not milled, good precision is unlikely to be observed even when a larger number of replicates are processed. Large heterogeneity will likely result in highly positively skewed distributions of measurements that cannot be accurately characterized by a small number of replicates (e.g., duplicates and triplicates).

4.3 Digestion mass and subsampling

In theory, fundamental error of a sample may be reduced by increasing the laboratory subsample mass for digestion and analysis. However, at concentrations on the order of parts per million, the amount of mass required for particles 2 mm in size to achieve reasonable precision will likely be impractical to process. Increasing the subsample mass from 0.5–2 g to

5–10 g can reduce the subsampling variability but will not necessarily satisfy measurement quality objectives for precision. USEPA Method 3050B (USEPA 1996a) recommends a digestion mass of 1 to 2 g and USEPA Methods 3051A and 3052 recommend a maximum of 0.5-g digestion mass (USEPA 2007, 1996b). Normal size acid digestion blocks used by most commercial environmental analytical laboratories can handle 5-g samples. However, because of potential foaming and loss of sample, 10-g samples may potentially be too large for standard digestion blocks. The recommendation is for digestion of a 5-g sample aliquot and, where or when practical, a 10-g sample aliquot.

If the sample is properly milled, then a single 5-g aliquot should be representative of the entire sample collected. However, we recommend that the sample aliquot be built using substantively the same incremental sampling approach used in the field whereby 20–30 increments are collected from the total sample to make up the sample aliquot. We recommend that the subsample mass and particle size reduction be adequate to ensure the fundamental error is no larger than 20–30%. Recent subsampling studies indicate that, even following milling, a sample exhibits significant heterogeneity such that a single increment is inappropriate for the digestion aliquot. Subsampling differences were evident between a random collection of 20 increments versus a systematic random sampling approach using a 2-dimensional Japanese Slab cake design. Thus, preparation of the digestion aliquot should entail collection of 20 increments from the milled sample using a systemic random sampling design, similar to what is conducted during field sampling.

4.4 Digestion

The standard digestion method, USEPA 3050B or 3051A (USEPA 1996a, 2007), is appropriate for most metals found at small-arms ranges, such as Cu, Pb, and Zn. The USEPA method 3050B procedure uses nitric acid (HNO_3) and hydrogen peroxide (H_2O_2). Environmental laboratories typically acid digest 0.5- to 2-g soil aliquots (subsamples). Briefly, one half gram of dried, ground, and sieved soil is placed in a digestion vessel to which 5 mL of 1:1 HNO_3 :reagent (e.g., deionized) water is added; and the mixture is heated at 95°C for 30 min. Note that the reagents are proportionally increased for larger dry-weight masses (e.g., 10 mL of 1:1 HNO_3 solution would be used to digest 1-g aliquots). Sequential additions, up to four, of 2.5 mL of concentrated HNO_3 are subsequently added until reaction ceases with 30 min of heating between each acid addition. After the

final nitric acid addition, the mixture is heated for 2 hr. The samples are allowed to cool to room temperature before 3 mL of 30% H_2O_2 is added, followed by heating for 15 min. Finally, 2 mL of H_2O_2 is added; and the mixture is covered with a ribbed watch glass and continuously heated until the volume of digestate is reduced to approximately 5 mL or heated at $95^\circ\text{C} \pm 5^\circ\text{C}$ without boiling for two hours. The digestate is then cooled to room temperature and filtered through a Whatman #40 filter and diluted to 50 mL with 1% HNO_3 . Analysis is then performed using USEPA Method 6010C (ICP-AES) or 6020A (ICP-MS) (USEPA 1996d,e).

If the samples are to be analyzed by ICP-AES Method 6010C (USEPA 1996d), then an additional step is needed. After the second 2-hr heating period, 5 mL of concentrated hydrochloric acid (HCl) is added to the digestion vessel with a final 15 min of heating. After cooling, the digestates are filtered and diluted to volume as described above.

Clausen et al. (2012b) evaluated whether increasing the digestion mass following milling improved precision of the results. Increasing the digested mass resulted in modest but statistically significant overall decreases in the variances for Pb and Sb. As discussed earlier, we recommend a digestion mass of 5 g; and where practical, 10-g would be better. Clausen et al. (2012b) also observed that increasing the digestion time improved metal recoveries although generally by less than 10%. Therefore, we do not generally recommend changes to the digestion interval unless the expectation is that the concentration of the metal of interest is likely to be near the action level.

One issue involving the sequential addition of concentrated HNO_3 needs addressing. USEPA Method 3050B calls for sequential additions of 2.5 mL of HNO_3 until the reaction ceases. Because the addition of varying amounts of acid changes the acid to soil ratio and the extraction efficiency, our recommendation is to standardize this step by requiring a total of 10 mL (i.e., 4×2.5 mL) of HNO_3 be added to all soil samples having a mass of 5 g. If a 10-g soil sample is to be digested, then the acid to soil ratio should be adjusted accordingly, thus requiring an addition of 20 mL of HNO_3 . The current approach outlined in EPA Method 3050B may lead to differing metal results, which are partially due to the digestion step rather than to the inherent metal content of the soil. For example, if the original sample had two additions of HNO_3 whereas the duplicate had four addi-

tions, it is very possible that the difference in metal results is a result of the different digestion process.

Another issue with the standard method is the poor recoveries of some metals, such as Sb and W. There may be other metals with poor recoveries as well, but these have not been explored. Consequently, when Sb or W are analytes of interest, separate, alternate digestion procedures are recommended for these two metals (Bednar et al. 2010a,b; Clausen et al. 2010b,c, 2007; Griggs et al. 2009, 2008; Hewitt and Cragin 1991; Kimbrough and Wakakuwa 1991). The alternate digestion procedure for Sb discussed below also appears to slightly improve recoveries for Pb. The method of instrumental analysis is the ICP-AES or ICP-MS USEPA Methods 6010C or 6020A (USEPA 1996d,e), respectively.

4.4.1 Antimony

USEPA Method 3050B often yields poor Sb recoveries, typically less than 50% (Nash et al. 2000; Hewitt and Cragin 1991; Kimbrough and Wakakuwa 1991). Poor recoveries are a result of insoluble Sb due to passivation and chemical bonding with the soil particles. The following digestion option (which is based on the procedure described in a footnote for Sb in USEPA Method 3050) improved recoveries for Sb.

- Using subsampling, weigh out 2 to 5 g of the soil sample into the digestion vessel.
- Add 2.5 mL of concentrated HNO_3 and 2.5 mL of concentrated HCl to the sample 2-g subsample (dry weight).
- Cover with a watch glass or vapor recovery device and reflux on hot block set at 95°C (covered container of water) for 15 min.
- While still hot, filter through an Ahlstrom 55 filter into a 100-mL vessel.
- Rinse the filter paper (while still in the funnel) with hot (about 95°C) 1.25 mL of concentrated HCl .
- Rinse 3 times with hot (95°C) reagent water (15-mL rinses), collecting the washings in the same digestion vessel.
- Place the filter paper and solid residue back into the original sample digestion vessel. Then add 2.5 mL of concentrated HCl , cover, and reflux on hot block for 20 min at $95^\circ\text{C} \pm 5^\circ\text{C}$ until the paper dissolves (typically less than 20 min).
- Remove the vessel from the heating source. Filter and rinse the filter paper with 5 mL of reagent water three times; rinse the cover and sides

of the digestion vessel with reagent water (combining all aqueous rinses with the filtrate). Allow the solution to cool, then dilute with reagent water to a final volume of 100 mL.

Preliminary testing of this method yielded improved Pb and Sb recoveries and significantly reduced the total variability (percent RSD) (Clausen et al. 2012b).

4.4.2 Tungsten

There are several different proposed W digestion methods, which are modifications to USEPA Methods 3050B and 3051A (USEPA 1996a,b) that appear to work equally well. The digestion procedure improves the solubility of W by preventing formations of insoluble polytungstates.

The first alternative method modifies the 3051A Method and includes adding phosphoric acid (H_3PO_4) to the digestion process and changing the composition of the solution used to rinse the filter media. The modified method uses 8 mL of concentrated HNO_3 and 2 mL of concentrated H_3PO_4 (both trace-metal grade) as the digestion solution for 2 g of milled soil instead of the 10 mL of HNO_3 specified in Method 3051A (USEPA 1996b). This change improved W recoveries from approximately 20% to 94% (Griggs et al. 2009; Griggs and Larson 2008). Unmodified digestion method recoveries are typically 10%–20% for W. Following digestion and filtration as described in Method 3051, the sample and filter paper were washed with a 2% concentrated H_3PO_4 solution. The volume of the digested sample was adjusted to 100 mL with ultra-pure water. Clausen et al. (2007) showed the unmodified method results in an underestimation of the W in the sample.

The second alternative to Method 3051A is similar to the above; in addition to 8 mL of concentrated HNO_3 and 2 mL of concentrated H_3PO_4 , 6 mL of H_2O_2 is used. The procedure resulted in W recoveries of 65%–112% (Griggs et al. 2009; Griggs and Larson 2008).

The third digestion procedure, developed by Bednar et al. (2010a,b), specifically focused on increasing the W recovery using Method 3050B. A 0.5-g aliquot of each of the solid samples was weighed into the digestion vessels and digested following the above described HNO_3 procedure with the modification of adding 1 mL of concentrated H_3PO_4 with the initial 5 mL of 1:1 HNO_3 :deionized water. If a larger mass is digested, then the

ratio of digestion acids needs to be increased proportionally. The digestate is then filtered and diluted as described above. Aliquots of the 50-mL digestate solutions are additionally diluted with 1% HNO_3 immediately prior to analysis, as needed, such that analyte concentrations are within the calibration range of the analytical instrumentation (generally 1:4 dilution). Elements such as Cr, Cu, Fe, K, Mg, Molybdenum (Mo), and Nickel (Ni) appear to have slightly larger extraction efficiencies by the H_3PO_4 procedure, compared to conventional digestion procedures, though the differences are generally less than a 10% increase (Bednar et al. 2010a).

A fourth tungsten alternative, which employs a modification to Method 3050B, is the following (Clausen et al. 2011). First, 0.5 g of soil is heated at 100°C in 5 mL of concentrated HNO_3 and 2 mL of 30% H_2O_2 ; this solution is evaporated to dryness. For larger masses, the volumes of the solutions should be proportionally increased. Once dry, 2 mL of concentrated HNO_3 is added to the digested soil; and the solution is again evaporated to dryness. Tungsten is recovered from the digested soil by dissolving the digestate in 2 mL of 20% ammonium hydroxide (NH_4OH) followed by sonicating and vortexing to ensure mixing. Once complete, 20 mL of a 2% NH_4OH /1% ethylenediamine tetraacetic acid (EDTA) solution is added; and the resulting solution is filtered and diluted significantly (51 times with a 0.2% NH_4OH /0.1% EDTA solution) prior to analysis. Use of NH_4OH and EDTA in the final extraction steps is necessary to maintain W in soluble forms prior to analysis.

4.5 Quality control

Our proposed revision for Method 3050B includes a matrix spike after grinding is done. Matrix spike duplicates (MSDs) are not needed to evaluate precision. Total measurement precision is evaluated via a set of independent replicate incremental samples. Lab precision is evaluated via lab subsample replicates (e.g., triplicates). Available performance data for ground LCSs and method blanks are discussed in Sections 5.2 and 5.3. One half the reporting limit requirement for blank contamination, while viable for reagent and instrument blanks, will generally not be viable for ground method blanks prepared from materials such as sand or glass as these materials generally contain variable levels of native metals. The use of upper tolerance limits (UTLs) for ground blanks is discussed in Section 5.3.

A “clean soil” spiked with small (less than 2 mm) particles of Pb, Sb, Cu, and Zn can be purchased from Environmental Research Associates (ERA) and potentially processed as an LCS for a batch of ISM samples from small-arms ranges. The solid standard from ERA contains Pb and Sb at 400 mg/kg and Zn and Cu at 1000 mg/kg. However, if other metals are also potential contaminants of concern for the project, this ERA standard alone will likely not suffice as an LCS. Owing to insufficient data, statistical acceptances for the recoveries of the four metals have not been established (e.g., for comparison with in-house laboratory statistical control limits). The low-level LCS is digested and analyzed with the environmental samples. The recovery of the low-level LCS should be 70%–130%.

We recommend that the following protocols outlined in EPA Method 3050B are followed for any project. The protocols include triplicate laboratory subsamples, which should be collected and digested with each batch of environmental samples to evaluate laboratory precision. The RSD for the triplicates should be calculated.

A matrix spike should be prepared according to the frequency described during the project planning stage of the project (e.g., one batch of environmental samples) by spiking a subsample with the analytes of interest following milling but *prior to* digestion and analysis. If the matrix spike is prepared from the same environmental sample as the laboratory triplicate, calculate the matrix spike recovery using the mean of the triplicate analyses. Owing to the large sample mass (1–2 kg) and heterogeneity (e.g., when metal fragments are present in the sample), it is typically undesirable to prepare the matrix spike prior to steps 7.1.1–7.1.8 of EPA Method 3050B.

A limit of detection (LOD) check sample should be prepared according to the frequency described during the project planning stage of the project. The LOD check sample is a clean matrix spiked with all of the analytes at concentrations less than the limit of quantitation but large enough to consistently produce detectable results. The LOD is digested and analyzed with the environmental samples.

4.6 Method blanks

The optimal approach to prepare method blanks for ISM-based metals analysis is a topic of on-going research. Factors, such as the metals of interest, the concentrations of interest in the environmental samples, and

the composition of the milling surfaces, need to be considered on a case-by-case basis. To date, method blanks of both Ottawa sand and glass (glass beads and laboratory glassware) have been milled and subsampled using substantively the same procedure in Method 8330B.

Glass used to prepare method blanks needs to be initially finely milled and subsequently acid washed prior to being milled a second time with the ISM samples. Glass beads were washed with aqua regia, a 1:3 solution by volume of concentrated HNO_3 and HCl (trace grade for each). The acid solution was added to a jar containing the glass beads and swirled for approximately 1 min. The acid was then decanted and the glass beads rinsed with deionized water three times, decanting the deionized water after each rinse.

5 Case Study: Application of Incremental Sampling Methodology at Small-arms Ranges

5.1 Field samples

Studies in which ISM soil samples from small-arms ranges were milled using a ring puck mill (five 60-s cycles) and subsampled using substantively the same procedures described in Method 8330B indicate that the ring puck mill can successfully be used to process samples for Pb, Sb, Zn, and Cu (Clausen et al. 2013, 2012b). These four metals were evaluated because they are typically the primary munitions constituents of interest for small-arms ranges. For the purposes of illustration, a study conducted to compare “conventional” sampling using grab (discrete) samples with samples collected using the ISM is summarized below. More details can be found in Clausen et al. (2013, 2012b).

Following a “grid-node” sampling approach (i.e., systematic sampling), Clausen et al (2013, 2012b) collected from the face of an impact berm 30 individual grab (discrete) surface soil samples from a depth of 0 to 5 cm using a 2-cm CMIST corer and placed them in 4-oz jars. Each of these samples consisted of approximately 200 g of material. The soil samples were air-dried at ambient temperature, sieved to remove the greater-than-2-mm fraction, and the less-than-2-mm portion was disaggregated in a mortar and pestle for 1 min. Typically, most commercial environmental laboratories do not air-dry soil samples. In addition, disaggregation of the sample is not typically performed, even though it is an option in the method, unless the laboratory is specifically instructed to perform disaggregation. No further processing of the sample was done prior to digestion. The subsample used for digestion consisted of 2 g of material scooped from the top of the 4-oz jar. The digestion procedures followed USEPA Method 3050B. After digestion, the samples were instrumentally determined by ICP-AES using USEPA Method 6010C.

Using systematic random sampling, this study also collected a set of seven individual replicate ISM soil samples from the same DU as the grab samples. Each ISM sample was prepared by collecting 100 increments using the CMIST sampler and consisted of approximately 1 kg of material. The

ISM samples were air-dried and sieved at the laboratory using a #10 (2 mm) sieve. The less-than-2-mm size fraction was ground in a puck mill for 300 s with a 60 s cooling step between milling intervals and then evenly spread onto an aluminum cookie sheet for subsampling. The greater-than-2-mm size fraction was weighed and set aside. Twenty increments (i.e., small aliquots of milled soil) were collected randomly with a spatula and combined to prepare 2-g subsamples for digestion and subsequent analysis by ICP-AES.

As shown in Tables 4 and 5, the repeatability of the ISM was far greater than the “conventional” approach using grab samples (Clausen et al. 2012b).

Table 4. Descriptive statistics for set of $n = 30$ grab (discrete) samples from a small-arms range Decision Unit.

Statistic	Cu (mg/kg)	Pb (mg/kg)	Sb (mg/kg)	Zn (mg/kg)
Mean	300	5,060	87.8	66.1
Median	270	1,238	10.0	61.9
Min	69.8	43.9	0.898	35.8
Max	598	79,020	2,072	111
STD	132	14,438	375	17.6
%RSD	44	285	427	27

Min—minimum; Max—maximum

STD—Standard Deviation

%RSD—Percent Relative Standard Deviation

Table 5. Descriptive statistics for set of $n = 7$ incremental samples consisting of 100 increments from a small-arms range Decision Unit.

Statistic	Cu (mg/kg)	Pb (mg/kg)	Sb (mg/kg)	Zn (mg/kg)
Mean	648	2,929	22.8	81.8
Median	609	2,638	20.7	78.2
Min	413	2,490	19.5	65.2
Max	882	3,595	28.9	95.9
STD	169	490	3.79	12.1
%RSD	26	17	17	15

Min—minimum; Max—maximum,

STD—Standard Deviation

%RSD—Percent Relative Standard Deviation

The RSDs for the Pb and Sb replicate ($n = 30$) discrete samples were about one order of magnitude greater than the corresponding RSDs for the replicate ($n = 7$) ISM samples. After the grab and incremental sample results were logarithmically transformed to normalize the distributions, the grab Pb and Sb variances were significantly larger than the corresponding incremental sample variances (at the 95% level of confidence by the F-test and Levene's test). Significant differences were not observed for Zn and Cu.

Spurious cross contamination for these four metals from the puck mill also seemed to be negligibly small for the ISM samples. The smaller RSDs for the ISM samples are largely owing to the particle-size reduction that resulted from the milling in the puck mill. When the samples are not milled, RSDs of the order of 100% have also been observed for Pb in ISM samples from small-arms ranges even if subsampling is done using a rotary splitter. Milling with the puck mill is not only important for reasonable repeatability but is especially convenient when both explosives and small-arms metals are of interest because (after milling) a single ISM sample may be subsampled for the subsequent analysis of metals and explosives

Excellent repeatability was also obtained for soil collected from a small-arms range using ISM when the soil was ground using a roller mill (US Stoneware roller mill, Model 803FVM) with 1-gal. polyethylene-lined steel cans and agate grinding stones (Clausen et al. 2012b). An incremental sample from a small-arms range was prepared by collecting and compositing 200 increments from an impact berm, yielding a 25-kg sample. The incremental sample was air-dried at ambient temperature and passed through a 2-mm sieve. A rotary splitter was subsequently used to prepare seven splits from the sieved portion of the material (i.e., the less-than-2-mm fraction) that were subsequently analyzed by three different laboratories (CRREL, Test America, and APPL Inc.). Two splits (used as "controls") were not milled. The other splits were milled using (1) mortar and pestle, (2) the roller mill and (3) three different puck mills using five 60-s cycles. The split for the roller mill was ground for 18 hours. Fifteen laboratory replicates were analyzed for each split. For quality control purposes, CRREL also analyzed a duplicate set of 15 laboratory replicates after the split was milled in a puck mill. Except for the milling equipment, each set of 15 laboratory replicates was processed (e.g., subsampled, digested, and analyzed) in the same manner. Table 6 summarizes the RSDs for each set of 15 replicates.

Table 6. Processed with different milling equipment, RSDs of ISM splits from a small-arms range.

Equipment	Lab	Percent Relative Standard Deviation (%RSD) (<i>n</i> = 15 replicates)														
		Al	Ba	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Sb	Sr	V	Zn
Unground #1	TA	4	5	ND	5	5	257	4	NA	4	7	61	116	NA	4	162
Unground #2	CRREL	2	15	2	2	5	25	1	1	1	2	39	69	4	NA	17
Mortar & Pestle	CRREL	5	5	ND	4	4	39	4	4	3	3	32	55	11	4	28
Puck Mill #1	APPL	5	6	ND	4	4	10	4	4	4	4	15	21	4	5	5
Puck Mill #2	CRREL	1	4	1	1	2	15	4	2	2	1	4	7	2	2	10
Puck Mill #2	CRREL	5	5	2	1	1	16	3	3	2	2	4	5	5	2	11
Puck Mill #3	TA	6	6	ND	5	5	5	4	5	5	5	5	8	NA	5	6
Roller Mill	TA	1	1	ND	1	1	3	1	1	1	1	1	8	NA	1	2

NA—Not Analyzed; ND—Not detected.

Bolded values > 15%.

As shown in Table 6, large RSDs were obtained for the unground material. Better precision was obtained when the soil was ground using mortar and pestle. With some minor exceptions, the puck mill resulted in RSDs less than 15%. The roller mill resulted in the smallest RSDs for most of metals. It should be noted that implementation of the protocols in Clausen et al. (2013) for several of the field demonstrations described in this document resulted in performance objectives not necessarily met. In particular, higher than expected RSDs were evident for Cu, suggesting modifications to the ISM may be necessary in some cases. These modifications could include a longer milling interval, larger digestion aliquot mass, more subsampling increments, etc.

5.2 Laboratory control samples

In one (unpublished) study, two commercial environmental laboratories independently processed and analyzed the ERA standard using ISM. Each laboratory milled 500 g of the material in a puck mill and subsampled it using substantively the same approach described in Method 8330B. The two laboratories subsequently digested (Method 3050B) and instrumentally determined (Method 6010B) a set of 15 replicate 2-g subsamples for Sb, Cu, Pb, and Zn. The RSDs of the sets of metal results were less than 20%. The mean recoveries of Pb, Cu, and Zn ranged from 60 to 95%; but the mean Sb recovery was less than 10%. The low Sb recoveries may have been owing to (at least in part) a problem with the acid digestion procedure (e.g., insufficient volumes of HCl) rather than analyte losses during milling.

5.3 Method blanks

The Clausen et al. (2012b) study calculated (using ProUCL) the 99% UTLs for sets of replicate method blanks prepared from Ottawa sand and glass milled in a puck mill to measure the degree of blank contamination owing to the entire analytical procedure. UTLs, 99%, calculated from replicate method blanks can be used as “detection limits;” that is, detectable concentrations would be reported for environmental samples when the analyte concentrations in the samples are greater than the 99% UTL of the method blanks (Georgian and Osborn 2004).

5.3.1 Ottawa sand

The UTLs for the Ottawa sand blanks were on the order of 10 mg/kg for Pb, Cu, Zn, and Sb (as well as for several other metals, including Ni and Ba) and were discussed in Georgian and Osborn (2004). However, significantly larger 99% UTLs were calculated for some metals (e.g., about 100 mg/kg for Cr and Mg and about 1000 mg/kg for Fe and Al). The results suggested that Ottawa sand method blanks may be appropriate for incremental soil samples collected from small-arms ranges if the decision limits for Pb, Sb, Cu, and Zn are on the order of at least 100 mg/kg.

5.3.2 Glass

Method blanks prepared from glass produced variable results (Clausen et al. 2012b). Metals were detected at relatively low concentrations when the glass blanks were not milled prior to analysis. However, after the blanks (glass beads) were milled, the mean concentrations of a number of metals increased by one to two orders of magnitude owing to a combination of contamination from the puck mill and increases in the surface area, which increased the concentration of soluble metals during the acid digestions. For example, milling increased the mean concentration of Pb for one set of replicate blanks from about 0.1 to 1 mg/kg and the mean concentration of Zn from 20 to 500 mg/kg. For some metals, the surface area increase (owing to milling) resulted in elevated 99% UTLs that were strongly dependent on the source of the glass beads. For example, glass purchased from two different sources produced 99% UTLs for ground Sb blanks that differed by about one order of magnitude (about 10 mg/kg versus about 100 mg/kg). The 99% UTLs for the ground Zn blanks ranged from 100 to 1000 mg/kg. It was concluded that glass may not be a desirable material to prepare method blanks unless the glass is initially finely milled and subse-

quently acid washed prior to being milled a second time with the environmental incremental samples.

Table 7 summarizes the results for analyses of 5-mm glass beads (Kimble Kontes, No. 13500-5) as reported in Clausen et al. (2012b). Descriptive statistics are presented for unwashed glass beads that were not milled, acid-washed glass beads that were not milled, unwashed glass beads that were milled, and glass beads that were milled and subsequently acid washed. The unground glass beads contain detectable levels of metals (Table 7). The glass beads were washed with aqua regia, a 1:3 solution by volume of nitric acid and hydrochloric acid (trace grade for each). The acid solution was added to a jar containing the glass beads and swirled for approximately 1 min. The acid was then decanted and the glass beads rinsed three times with deionized water, decanting the deionized water after each rinse. As shown in Table 7, the metal concentrations for the washed and unwashed beads are relatively low (e.g., about 1 ppm or less). As expected, the concentrations of the unwashed beads that were not milled are slightly lower than the acid-washed glass. Milling increased the metals concentration overall (e.g., by over an order of magnitude for some metals) owing to cross-contamination from the milling equipment (e.g., Fe and Cr) or to the increased surface area of the glass beads. However, for most of the heavy metals, the mean concentrations of the milled, washed glass were less than 1 mg/kg.

Table 7. Metals results for unground glass beads; unground, washed glass beads; ground glass beads; and washed, ground glass beads.

Treatment	Statistic	Concentration (mg/kg)														
		Al	Ba	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Sb	Sr	V	Zn
Unground Glass	n	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
	Mean	2.84	0.153	ND	ND	0.020	1.20	2.87	7.21	0.075	0.033	0.135	0.045	0.078	ND	0.603
	Median	2.84	0.153	ND	ND	0.020	1.20	2.87	7.21	0.075	0.033	0.135	0.045	0.078	ND	0.603
	Min	2.45	0.140	ND	ND	0.010	1.16	2.55	6.48	0.075	0.020	0.085	0.030	0.075	ND	0.520
	Max	3.22	0.165	ND	ND	0.030	1.25	3.19	7.94	0.075	0.045	0.185	0.060	0.080	ND	0.685
	STD	0.544	0.018	ND	ND	0.014	0.064	0.453	1.03	0.000	0.018	0.071	0.021	0.004	ND	0.117
	%RSD	19	12	ND	ND	71	5	16	14	0	54	52	47	5	ND	19
Unground Glass Washed	n	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
	Mean	2.01	0.095	ND	ND	ND	1.18	1.84	5.38	0.023	ND	0.063	ND	0.050	ND	0.407
	Median	1.93	0.100	ND	ND	ND	1.19	1.85	5.43	0.025	ND	0.065	ND	0.050	ND	0.445
	Min	1.87	0.085	ND	ND	ND	1.15	1.73	4.99	0.020	ND	0.055	ND	0.050	ND	0.225
	Max	2.22	0.100	ND	ND	ND	1.22	1.96	5.73	0.025	ND	0.070	ND	0.050	ND	0.550
	STD	0.189	0.009	ND	ND	ND	0.035	0.115	0.372	0.003	ND	0.008	ND	0.000	ND	0.166
	%RSD	9	9	ND	ND	ND	3	6	7	12	ND	12	ND	0	ND	41
Ground Glass	n	18	18	15	18	18	18	18	18	18	18	18	18	18	18	18
	Mean	128	0.660	0.042	0.129	60.9	1.86	456	8.42	3.64	0.700	1.93	0.827	0.187	0.045	0.985
	Median	126	0.658	0.040	0.119	56.9	1.90	424	8.32	3.45	0.618	1.92	0.710	0.185	0.045	0.911
	Min	104	0.595	0.035	0.100	51.1	1.71	380	7.53	3.10	0.495	1.19	0.580	0.165	0.035	0.610
	Max	150	0.780	0.057	0.200	90.6	1.98	692	9.39	5.11	1.14	2.96	1.83	0.219	0.065	1.560
	STD	12.5	0.038	0.006	0.032	13.7	0.09	108	0.48	0.68	0.205	0.49	0.316	0.012	0.007	0.242
	%RSD	10	6	15	25	23	5	24	6	19	29	26	38	6	16	25
Ground Glass Washed	n	18	18	15	18	18	18	18	18	18	18	18	18	18	18	18
	Mean	30.0	ND	0.03	ND	4.86	1.56	27	4.60	0.357	0.722	0.470	0.040	0.078	ND	0.408
	Median	30.3	ND	0.03	ND	3.90	1.55	23	4.55	0.255	0.170	0.468	0.020	0.078	ND	0.393
	Min	22.3	ND	0.02	ND	2.92	1.40	17	3.60	0.205	0.010	0.240	ND	0.065	ND	0.220
	Max	37.5	ND	0.05	ND	10.4	1.96	52	5.40	0.900	3.74	0.780	0.175	0.095	ND	0.605
	STD	4.26	ND	0.01	ND	2.52	0.136	11.7	0.441	0.247	1.33	0.139	0.061	0.007	ND	0.103
	%RSD	14	ND	30	ND	52	9	44	10	69	184	30	154	9	ND	25

n—Sample size (replicates); Min—Minimum; Max—Maximum

%RSD—Percent Relative Standard Deviation; STD—Standard Deviation;

ND—Not detected (non-detects precluded calculation of some descriptive statistics)

6 Summary and Conclusions

We developed an ISM for metals in soils. To reduce distributional heterogeneity, at least 30–100 increments of roughly equal soil mass are collected randomly over the DU (e.g., using a coring device for cohesive soils) and subsequently combined to yield a 1–2-kg incremental sample. The objective of collecting a large number of small soil aliquots (increments) over the entire DU is to prepare a sample that contains the same proportions of analyte particles (e.g., in terms of sizes, shapes and compositions) as the DU's.

At the laboratory, each incremental sample is air-dried at room temperature for several days. Each dried sample is subsequently passed through a 2-mm (#10 mesh) sieve, and the two size fractions (less than 2 mm and greater than 2 mm) are weighed. The less-than-2-mm sieved fraction is mechanically milled (e.g., within a hood for dust control) using an appropriate grinder (e.g., one that does not introduce significant contamination from its grinding surfaces for the metals of interest), such as a puck mill or roller mill. Milling is typically necessary to reduce measurement uncertainty, especially when soils contain metal fragments, or the mean contaminant concentration is expected to be near an action level or other regulatory threshold. When characterizing metal contamination owing to small-arms range use, incremental samples can be ground with a puck mill (e.g., as described in Method 8330B). After grinding, the soil should appear as a uniform, free-flowing, fine powdery material. The ground material is subsequently spread onto a large tray as a thin slab of uniform thickness. To further minimize the subsampling error due to distributional heterogeneity, a number of small soil aliquots are collected randomly through the entire slab of ground material (e.g., using a flat-bottom plastic spatula) to obtain an adequate subsample mass (e.g., 2–10 g) for digestion and subsequent instrumental determination.

Results indicate that systematic random sampling using ISM resulted in significantly lower variances for Pb and Sb than conventional grab sampling for soils containing metallic particles (Clausen et al. 2013, 2012b.). There appeared to be no differences in practical significance for Zn and Cu as these metals did not exhibit large heterogeneity for the grab samples. (e.g., that is typically observed when bullet fragments contain these met-

als). ISM decreased by at least one order of magnitude the measurement uncertainty of metal concentrations of most munitions constituents in soils collected at small-arms ranges. One drawback to using ISM is when subsurface soil samples are needed. The ISM approach greatly increases the labor required to obtain a sufficient number of increments per sample.

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14. ABSTRACT Heterogeneous distribution of metallic residues in surface soils creates unique challenges for collecting soil samples that provide representative and reproducible results. In particular, soils containing metal fragments at military training ranges, such as small-arms ranges, are especially problematic to analyze owing to their large compositional and distributional (i.e., spatial) heterogeneities. The recognition of the heterogeneous nature of energetic residues in surface soils at military training ranges resulted in significant changes to the field sampling and sample processing procedures for energetics as described in United States Environmental Protection Agency (USPEA) SW-846 Method 8330B. The incremental sampling methodology (ISM) of Method 8330B for energetics was modified to develop a similar approach for metals. The approach has been successfully implemented to analyze surface soils with metallic residues at several active and inactive military training ranges. In most cases, ISM produced results more representative and reproducible than results from conventional grab (i.e., discrete) sampling and analysis procedures for surface soils collected from small-arms ranges containing metallic residues.					
15. SUBJECT TERMS Antimony Copper		Decision Units Incremental sampling methodology (ISM) Lead		Metals Ranges Surface soil	
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